Polymer Photovoltaics – Challenges and Opportunities

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ABSTRACT

A new generation of photovoltaic materials, the so-called Third Generation Photovoltaics, has the potential to significantly lower costs primarily because of the use of much simpler manufacturing processes. Third Generation PV, which includes dye sensitized titania (DSSC) technology, hybrid technology and polymer/nanoparticle composites, has the potential for realizing lower cost due to lower materials costs and low cost manufacturing processes, such as high speed, continuous roll-to-roll/laminating processes, without vacuum deposition. Along with low cost potential, the feature set inherent in polymer PV opens new market applications.   With this promise, significant work remains, thereby opening the door to innovation and commercial success.

1. Definitions

We define flexible PV as either DSSC or polymer/nanoparticle composites on a transparent polymer substrate and superstrate. DSSC technology requires the use of an electrolyte to shuttle charge between the counter electrode and the sensitizing dye. The so-called Hybrid cell is defined as the combination of dye sensitized titania with a conducting polymer substituting for the electrolyte. The polymer/nanoparticle PV will be referred to simply as the polymer cell or polymer PV. Since these three technologies are variations on similar themes, we suggest that they can be thought of as a continuum of overlapping materials with similar functions.
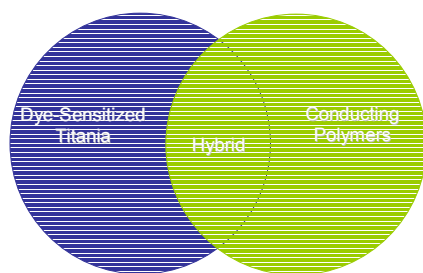

Figure 1: Intersection of third generation technologies

2. Dye-Sensitized Titania Cells

Dye-sensitized solar cells (DSSCs) incorporate two substrates at least one of which has been coated with a transparent conducting oxide (TCO), referred to as the primary electrode and the other, the counter electrode, coated with TCO or a non-corrosive metal such as titanium upon which is coated a very thin layer of platinum. A porous layer of a semiconductor such as TiO_2 is deposited on the conductive surface of the TCO.

This porous layer is then coated by dye so that it is made sensitive to visible radiation. To be optimally effective, the dye concentration must be limited to a monolayer of dye molecules. Electrolyte, which contains the redox couple I-/I3-, is imbibed into the titania layer. To complete the cell, the substrate baring the primary electrode and the sensitized titania layer is brought into face-to-face contact with the counter electrode. Refer to Figure 2.

The highly porous semiconductor provides very high surface area which allows a very high concentration of dye to be absorbed on it which in turn allows for very high light absorption [1]. When light enters the titania layer, it is absorbed by the dye molecules which undergo a transition to an excited state. The excited dye molecules then inject electrons into the titania; the electrons migrate through the titania until they reach the TCO. The electric current thus produced is passed into an external circuit to perform electrical work. Electrons re-enter the cell though the counter electrode and are transferred to the electrolyte via a reduction reaction in which I3- (tri-iodide) is converted to I- (iodide ion). The iodide ions transport electrons to the oxidized dyes (D+) on the semiconductor where they are transferred to the dye molecules thus completing the electrical circuit.
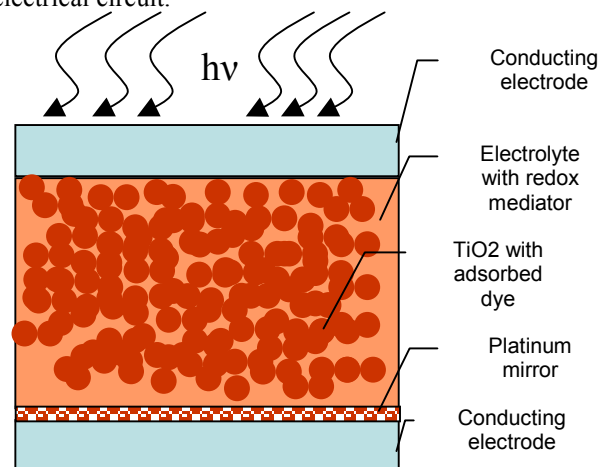

Figure 2: Schematic of DSSC

The best performance of the DSSC photocell is approximately 11% as reported by the EPFL and others [2].

3. Polymer/nanoparticle Composite Cells

In polymer cells there are two electrodes, a photoactive layer, and an auxiliary hole carrying layer. In some cells, an auxiliary electron carrying layer is inserted between the photoactive layer and the metal electrode. One of the electrodes must be a transparent semi-conductor (e.g., ITO) and the other is a metal coating. Refer to Figure 3.

The active layer in polymer cells has two components: a light absorber and a nanoparticulate electron carrier. The light absorber is a p-type polymeric conductor, such as a

poly(phenylene vinylene) or poly(3-hexylthiophene). The polymer has three functions: 1] it absorbs light; 2] it transfers electrons to the electron acceptor/carrier; 3] it carries holes to the ITO electrode. The electron acceptor has two functions: 1] it accepts electrons and 2] it transfers the electrons to the aluminum electrode. The best choice for the latter is a derivative of fullerene, e.g., PCBM, as shown in Fig. 3.

A key to higher performance centers on control of the morphology of phase separation. It has been shown that a bilayer structure of the same two components exhibits very poor cell performance [3]. This is due to the fact that the lifetime of the excited state of the dye (exciton) is shorter than the transfer rate of the exciton to the interface. As a result, the great majority of the excitons formed in the bulk of the polymer layer are annihilated before they migrate to the interface and transfer electrons to the acceptor.
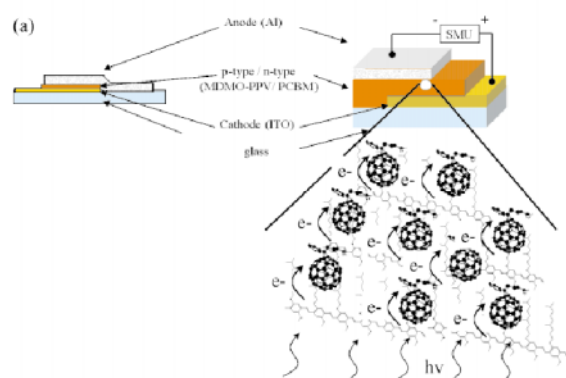

Figure 3: Schematic of Polymer cell with electron hopping

Phase separation which forms a bulk heterojunction morphology (Fig. 5) exhibits far better performance that the bilayer. In this morphology (Fig. 4) the absorber and electron acceptor are in intimate contact throughout the entire active layer [4, 5]. The exciton path length is shorter than its lifetime and electron transfer is much more likely.
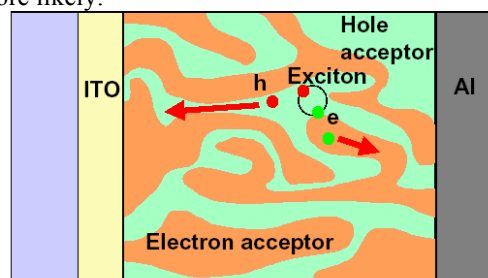

Figure 4: Schematic of bulk heterojunction

Recently, it was discovered that various post-processing treatments raise the performance by as much as 50% above that of an untreated sample. The best efficiency obtained for the latter is 3.5%. The reason for this improvement is not yet understood.

There are several obstacles that must be overcome before this technology reaches its full potential, one of which is incomplete absorption of the incident radiation.

The polymeric dyes exhibit high extinction coefficients (>100,000), but due to low exciton migration rates, the films must be thinner than 100nm which significantly contributes to incomplete absorption. Another obstacle is the underutilization of the available solar energy due to the narrow absorption bandwidth of the polymer. We estimate that approximately 40% of the light (nearly all of the wavelengths from about 600nm out into the near IR) is wasted. Another obstacle in the polymer system is charge mobility.

4. Hybrid Cells

As the name implies, hybrid cells are a mix of two technologies. they comprise dye sensitized titania coated and sintered on a transparent semi-conducting oxide, and a p-type, polymeric conductor, which carries electrons from the counter electrode to the oxidized dye. Since the one polymer replaces the multi-component electrolyte the cells are expected to be far simpler to make reproducibly and should afford the same or similar form factors as the polymer PV type cells.

This technology, like that of the polymer cell, has not yet advanced to the performance level of that of the DSSC technology. The efficiency values are in the single digits range. One of the causes of low performance is incomplete filling of the small cavities in the titania nanoparticles [6].

5. The Three Legged Performance Foundation

Successful PV technology must, for its target market, satisfy three technical objectives – efficiency (η), lifetime (τ), and manufacturability (π) – and how these objectives are all connected.
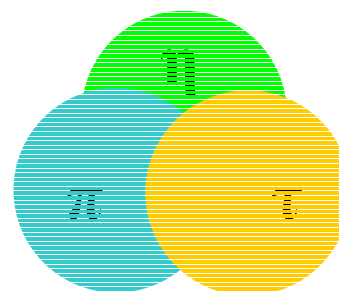

Figure 5: The three legs: efficiency, life and cost

Crystalline silicon cells and their variations trace their roots to the mid-'50s. Initial market introduction of silicon solar panels had less than 4% efficiency. Although it required several decades of intense development activity, this technology is currently produced in high volume at efficiency values well over 15%. Yet the market does not always demand such high efficiency, as witnessed by the entry of relatively low efficiency thin film products.

Years of field experience with many technologies has given us incontrovertible evidence that PV technology can be made to last for decades, even in severe climates. Indeed, the conclusion that many have drawn from this experience is that the "package" is the weak point – not the solar cell. To date, most PV technologies have been

"packaged" for multi-decade service life. This has been done, in part, to extend the timeframe of levelized energy cost calculations to help support the initial high capital cost associated with buying PV. Yet, many applications have a mission life of less than 20 years; some as short as a matter of months.

Manufacturability broadly encompasses yield, return on capital (or, capital depreciation per unit produced), and throughput. Although quasi-continuous processes are used in manufacturing PV, the production lines consist of multiple machines with throughput defined in terms such as hundreds of wafers per hour or m^2 per hour. Employed capital for crystalline silicon and deposited thin films, as reported in the press, is typically well above $1 million for each MW of annual production capacity. Converted into an effective capital burden per shipped-watt, this is one of the higher components of overall manufacturing cost.

4. The Opportunity

Polymer PV technology offers an opportunity for successful integration of the three objectives and the penetration of multiple markets in the not too distant future.

Beginning with efficiency, the reported AM 1.5 efficiency for a dye-sensitized cell record is 10.4% [2]; The highest known efficiency for a polymer cell is ~3.5% [7], although (Fig. 6) models of plausible performance of polymer cells suggest that efficiency above 15%, indeed up to 30%, are ultimately possible. Both were laboratory scale devices, constructed for optimum performance without regard to the other two legs. Most researchers in the filed believe that modules comprising these materials are capable of being produced at efficiencies well above 15%. Government agencies, such as DARPA, are beginning to fund research with performance goals in this range.
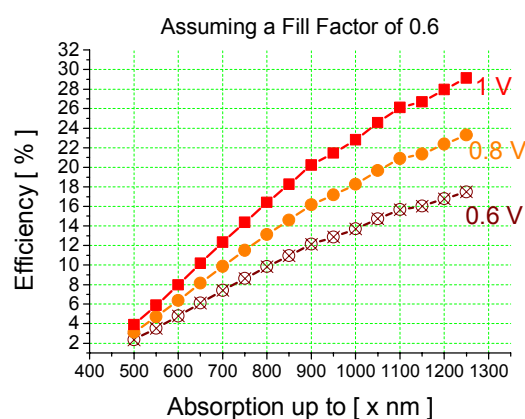

Figure 6: Polymer cell efficiency (model)

Polymer PV technology offers a path to successful integration of the three objectives for multiple, though perhaps not all, markets in the foreseeable future.

Beginning with efficiency, the reported AM 1.5 efficiency for a dye-sensitized cell record is 10.4% [3]; ~3.5% for a polymer cell.   Both were laboratory scale devices, constructed to achieve efficiency, without regard to the other two legs. Theoreticians and scientists in the field, however, believe that production modules well above 15% are plausible.

Estimates of greater than ten year lifetime for dye-sensitized cells have been based on accelerated stress tests; dye cells have not been in the field long enough to suggest otherwise.   What is well understood, however, is the influence that the "package" has on the service life.

PV modules with flexible superstrates, i.e., plastic, with warranties up to 20 years are commercially available. Highly flexible modules are also available, though these are offered with substantially shorter warranty terms. In effect, by constructing modules with polymeric superstrates, the mission life of the product can be "designed in" to offer the customer their service life / product price requirements.

Polymer PV can be produced by coating and printing substrates with suspensions and fluids without vacuum. By restricting the process to relatively low temperature, i.e., below 150 °C, relatively inexpensive polymer substrates can be used. When continuous coating methods are used, such as those that are employed in manufacturing photographic negative film, roll-to-roll manufacturing can be used. With innovation in cell-to-cell interconnection, the series connection of cells can take place in the roll-to-roll process, as the superstrates and substrate, with the active material in between, are joined together. With additional innovations in post processing, the PV roll can be cut to length to provide cells of the correct area for the specified current and cut to width to provide the number of cells in series for the specified voltage. One roll yields many products. Because the roll-to-roll manufacturing through-put is measured in linear meters per minute and because the equipment can readily be adapted from other industries, the employed capital per watt is a factor of 10 to 20 lower then that for crystalline silicon or deposited thin films.

5. Intermediate Conclusion

The manufacturing cost fundamentals of polymer PV are attractive. Modules produced with polymer PV can be designed to meet the mission life of the application while providing desirable physical attributes, such as light weight, flexibility and ruggedness.

Nevertheless, the state of the art in polymer PV is only just beginning to achieve the minimum level of performance necessary for broad market entry. There is work to be done.

6. Technology Roadmap

The objective of the technology roadmap is to outline a path for commercialization of polymer PV within a framework of step-by-step advances in materials and processes, all in the context of roll-to-roll manufacturing. With the performance of the dye-sensitized cell (DSSC) well ahead of the polymer cell, the roadmap is based on staged commercialization: DSSC followed by hybrid, followed by polymer cell.

The quest for efficiency is common to all PV technologies, as efficiency has a direct impact on the bottom line. The Roadmap considers the drivers of efficiency and outlines development paths to address them. The factors are well known: light management, internal resistance and band gap.

The DSSC offers unique opportunity to tune the dye chemistry to achieve greater absorption of light (as characterized by the extinction coefficient) and over a broader range (spectral sensitivity). The extinction coefficient of today's dye is below 15,000 whereas there is reasonable expectation that an extinction coefficient of 100,000 or more is plausible. With a greater extinction coefficient, the absorbing layer can be made thinner with no loss in absorbed light, while reducing the series resistance.

Internal series resistance comes from the electrodes and cell chemistry. With respect to electrodes, as with other PV films, the optimum would be highly conductive, transparent and mechanically robust electrodes. Given the polymeric substrate, the choices for top electrode are limited, with preference falling to indium tin oxide (ITO). Not only is this a compromise, but it is also, within the context of a low cost technology, a major cost component.

Performance of the polymer cell, like other solar cells, is dependent on absorbing as much light as possible, converting the photon energy in to free electrons, getting the electrons out and minimizing resistance. In order to increase the amount of light that is useful, the absorption must increase (Fig. 7, Arrow 1 below). Other than sensitizing the polymer with a dye, the polymer can be made thicker. Unfortunately the mobility of existing polymers and nanoparticles causes a reduction in total efficiency as the layer becomes thicker.

In order to absorb more of the spectrum (Fig. 7, Arrow 2 below), the band gap of the polymer must be lower, without sacrificing electron transfer. New polymers, with lower band gaps, are in order.
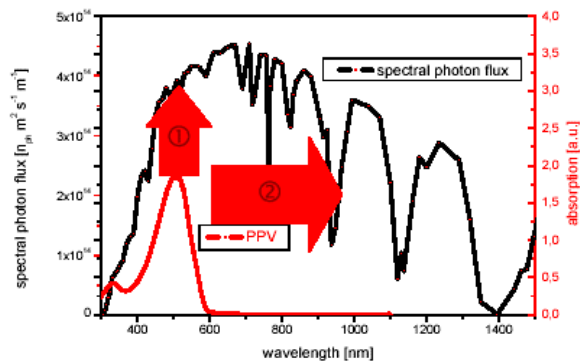

Figure 7: Absorption of polymer vs. solar spectrum

Because of the spatial and surface relationships between the absorber, electron carrier and hole conductor, the actual morphology of the constituents is key. Morphology can be manipulated, though the optimum is elusive.

Finally, there is an option to be considered in using blends of different polymers – each designed to absorb a specific range of light; theses layers can be integrated into a multiplayer device – either one layer uniformly atop the other or layers that are actually mixed together.

The hybrid cell takes advantage of both the dye sensitized and polymer cells, addressing the weaknesses of each. Hole mobility is key, as are rheology (to get into the porous structure) and the electrode conductivity.

Table 1 summarizes key areas of research that will be essential to successful commercialization of polymer PV.

Light management	• Enhanced absorptivity of dyes • Low bandgap polymers
Reduce series resistance	• Higher mobility polymers • Enhanced TCOs • Electrolyte formulations • Polymer morphology

Table 1: Summary of research areas for acceleration of the technology

7. Conclusion and Next Steps

The fundamentals of third generation PV, low cost materials, used in high-speed, roll-to-roll low cost processes, on low cost equipment, offer a compelling case for investment in advancing the technology and commercializing the resulting products. As with other PV technologies, there are multiple opportunities to gain significant improvement.

Given the enormous opportunity to leverage the features of this technology in emerging markets, as well as the opportunity for lower price points to rapidly expand existing markets, the authors encourage academic institutions as well as federal laboratories, especially NREL, to expend their existing programs and build new ones to innovate and develop technology components that serve to accelerate the advancement of the three legs.

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